METHANOL PRODUCTION FROM PARTIAL OXIDATION OF METHANE IN A SPECIALLY DESIGNED REACTOR

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Introduction

Research on direct partial oxidation of methane to methanol has last for a long time because of its great industrial potential. Unfortunately, in most literatures CH_3OH yield was always below 5%. The molecular of methanol is far more reactive than methane under similar condition. Methanol is easily oxidized to CO and/or CO_2. Therefore, the selectivity of methanol was always poor. Participation of catalyst has not improved methanol selectivity till now. The temperature and pressure for catalytic oxidation of methane were in the range of gas phase homogeneous oxidation. Then the gas phase homogeneous reaction was inevitable in the catalytic reaction. Therefore, it is necessary to continue the exploration on the gas phase homogeneous oxidation of methane.

Experimental

The gas phase partial oxidation of methane was investigated in a specially designed quartz lined tubular reactor. The quartz line was tightly fitted in the stainless steel line using an O-ring of fluoride rubber pressed by a locking nut to avoid contact of feed gas with metal wall so as to diminish the wall effect. And a spacer (quartz tube) was placed in the reactor to ensure the product mixture leave out the high temperature reaction zone rapidly so as to terminate the free radical reaction and minimize the deep oxidation of required product.

Results and discussion

In the specially designed reactor, a yield of CH_3OH about 7-8% (60-63% CH_3OH selectivity at 11-13% CH_4 conversion) could be obtained at 430-470°C, 5.0MPa and $CH_4/O_2/N_2$=100/10/10 (ml/min, STP), while O_2 was completely consumed. The selectivity of CO was about 30% and the selectivity of CO_2 was kept less than 5-10%. Production of H_2 was also observed, its concentration in the gas mixture was just less than that of CO. Since no HCHO was detected, it is believed that it decomposed quickly to CO and H_2 if it was formed in the reaction system.

In most literatures, high CH_3OH selectivity could be obtained when methane conversion was very low; however the selectivity would fall down quickly while increasing the methane conversion. The yield of methanol was always less than 5%. Comparison of the reaction conditions with that in our early work[1] and other literatures[2,3,4], the most difference lies in the reactor structure.

In order to verify what makes high methanol yield possible, some experiments were carried out by adjusting the structure of the reactor. Without O-ring for sealing the gap between quartz tube and stainless tube in the reactor, the methanol selectivity decreased sharply from 62% to 31%, and methanol yield fell from 8% down to only 3%. Instead of quartz line with silicate glass line, the selectivity only decreased slightly. The spacer (quartz tube) in the reactor does have some effect on the reaction because the methanol selectivity decreased from 62% to 41% (Table 1).

Table 1 Effect of the varying of the reactor structure on the partial oxidation of methane

Case*	Methane Conversion/%	Selectivity /%			Methanol Yield/%
		CH_3OH	CO	CO_2	
A	13.1	62.3	32.6	4.8	8.2
B	9.1	31.6	50.0	18.8	2.9
C	11.7	41.2	41.5	15.4	4.8
D	13.0	54.5	33.0	12.0	7.1

P=50atm, T=450℃, $CH_4/O_2/N_2$=100/10/10(ml/min)

*A-the original structure, B-without O-ring; C-without spacer; D-silicate glass line instead of quartz glass line

Conclusion

A yield of CH_3OH about 7-8% could be obtained in the specially designed reactor. It is supposed that the high CH_3OH yield should be attributed to the encapsulation of the ringed gap between the quartz line and the SS line. Higher CH_3OH selectivity could be achieved by improving the reactor design.

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